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Environmental Chemistry
Short CommunicationTHE OCTANOL/WATER PARTITION COEFFICIENT
OF METHYLMERCURIC CHLORIDE AND
METHYLMERCURIC HYDROXIDE IN
PURE WATER AND SALT SOLUTIONSMICHAEL A. MAJOR* and DAVID H. ROSENBLATT
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Abstract—The 1-octanol/water partition coefficient (K_{ow}) of methylmercury was determined at pH 7 in water and in aqueous solutions ranging from 0.0003 to 0.6000 M in sodium chloride. It was also determined over a pH range of 2 to 10 with a fixed sodium chloride concentration of 0.0045 M. In these experiments, K_{ow} was seen to increase with increasing chloride concentrations in the range 0.0 to 0.075 M and to decrease with increasing pH above 7. Results were similar whether low levels of methylmercuric chloride or methylmercuric hydroxide were used as the starting materials. Partitioning was not affected by changes in ionic strength.

Keywords—Octanol/water partition coefficient Methylmercury K_{ow}

INTRODUCTION

Mercury is found in many aquatic environments in the methylated form. Inorganic mercury can be methylated both by microorganisms and abiotically [1]. Mercury-contaminated freshwater systems usually contain both methylmercuric hydroxide and methylmercuric chloride, but in seawater the latter predominates [2]. Due to its lower polarity, methylmercuric chloride would be predicted to have a higher K_{ow} than the hydroxide [3] and also a greater rate of uptake by aquatic organisms [4]. The carbon-mercury bond is stable in methylmercury compounds, whereas anions associated with the metal exchange easily; thus, the relative concentrations of the chloride and hydroxide forms reflect environmental salinity [2], and addition of either methylmercuric chloride or methylmercuric hydroxide to buffered saline should result in very similar solutions.

Log K_{ow} values of 0.62 for mercury metal [5] and 2.26 for dimethylmercury [6] have been reported. In addition, a value for log K of 0.6 has

been found for the partition coefficient of methylmercuric chloride in the diethyl ether/water system [7]. However, a search of the literature has failed to find K_{ow} values for either methylmercuric chloride or methylmercuric hydroxide.

In this paper we present K_{ow} values for methylmercury(II) starting as the chloride and as the hydroxide. Values were determined at pH 7 in ultrapure water and at 13 different salinities. They were also determined at fixed salinity at nine different pH values.

MATERIALS AND METHODS

1-Octanol was obtained from the Aldrich Chemical Company (guaranteed purity 99%) and fractionally redistilled. Ultrapure water was purchased from New England Reagent Laboratory, and methylmercuric chloride and methylmercuric hydroxide were purchased from the Alfa Chemical Division of Morton Thiokol Corporation. Aqueous solutions of the two methylmercuries were prepared at 1,000 ppm. Solutions of each of the two were checked for purity by HPLC and diluted to 10 ppm with ultrapure water or with sodium chloride solutions of known concentration. The ultrapure wa-

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ter and the saline solutions that were used for all of the testing except the highest pH experiment were prepared with the appropriate buffer at a concentration of 0.01 M. The buffers used were: phosphate at pH 2, oxalate at pH 3, succinate at pH 4, acetate at pH 5, succinate at pH 6, phosphate at pH 7 and 8, and borate at pH 9 and 10.

The ultrapure water and saline solutions for the high-pH experiment were adjusted to pH 12 with NaOH and used without buffering. The effect of ionic strength on K_{ow} was tested by holding the salinity at 0.05 M and increasing the ionic strength with additions of NaClO₄. Perchlorate concentrations were 0.01 M, 0.05 M, 0.1 M and 0.6 M.

The concentration of mercury in octanol could not be assayed directly. To overcome this problem, the following procedure was used: Three aliquots of each aqueous test solution were removed for analysis, and three additional aliquots were extracted with equal volumes of octanol by shaking for 20 min. The mixtures were allowed to separate for 10 h, the octanol was removed, and the aqueous portions were analyzed. The concentration of methylmercury in an octanol extract was calculated as the difference in concentration between the original and octanol-extracted aqueous samples.

To ensure that the mercuric compounds were partitioning as expected, and that adsorption or other phenomena were not producing erroneous results, the octanol fractions from these experiments were pooled and back-extracted with four successive additions of pure water. Analyses of aqueous fractions and back-extracts were performed on a Beckman SpectraSpan V sequential plasma emission spectrometer. Calibration standards were prepared from stock solutions of mercuric chloride (Fischer Scientific) in water. The samples and standards were adjusted to 5,000 ppm lithium to obscure sodium or other metal emissions. The emissions of the samples at 253.652 nm were recorded and mercury concentrations calculated by interpolation.

RESULTS

The values of K_{ow} for methylmercuric species as a function of chloride concentration are shown in Figure 1. Pairwise comparisons between the K_{ow} means, when either methylmercuric chloride or methylmercuric hydroxide was used as the source of methylmercury, show no statistically significant differences ($p > 0.10$), according to the Student's *t* test. The mean K_{ow} was 0.07 ± 0.05 in

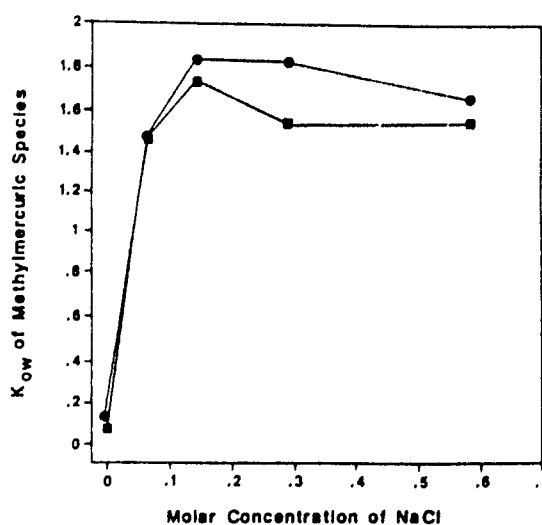


Fig. 1. The octanol/water partition coefficients of methylmercuric hydroxide, ●, and methylmercuric chloride, ■, in pure water and in 0.075 M, 0.15 M, 0.30 M and 0.60 M NaCl.

ultrapure water and increased to 1.7 ± 0.2 at chloride levels above 0.075 M. Subsequent experiments with methylmercuric hydroxide in the salinity range up to 0.037 M NaCl reveal a zone of nearly linear increase in K_{ow} with salinity between 0.0000 M and 0.0047 M NaCl. At higher levels, increases in salinity produced smaller changes in K_{ow} (Fig. 2).

Increase in pH of the system from 2 to 6 had lit-

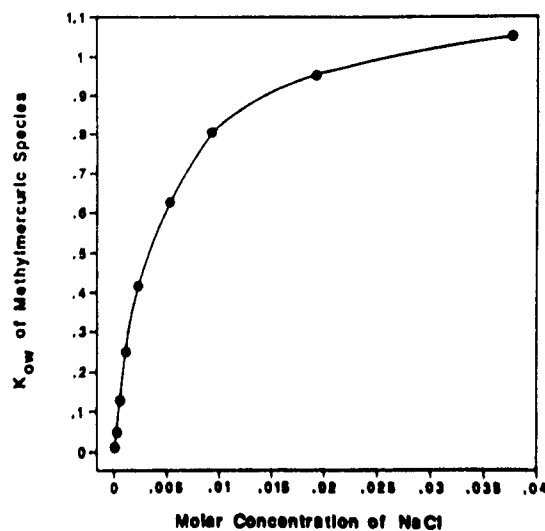


Fig. 2. The octanol/water partition coefficients of methylmercuric hydroxide in the salinity range 0.0000 to 0.0037 M NaCl.

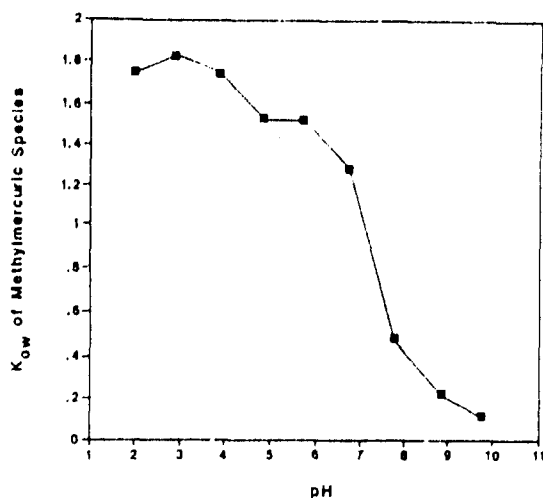


Fig. 3. The octanol/water partition coefficients of methylmercuric chloride in the pH range of 2 to 10 at a fixed salinity of 0.0045 M NaCl.

the effect on K_{ow} , but further increases caused a sharp decrease in K_{ow} (Fig. 3). Samples at pH 12 containing 0.001 M and 0.01 M NaCl had K_{ow} s statistically indistinguishable from those of pure water.

An additional experiment was designed to assess the effect of changes in ionic strength. Raising the ionic strength of a 0.0047 M chloride solution with potassium perchlorate in the ionic strength range of 0.01 M to 0.6 M did not affect the partitioning behavior.

Back-extractions of octanol pooled from these experiments confirmed that the octanol contained a quantity of mercury consistent with that lost from the water and salt solutions through partitioning.

DISCUSSION

The salinities chosen in this study approximate the range of chloride concentrations encountered in natural ecosystems. Altman and Dittmer [8] report a chloride level of 8 ppm (0.0002 M) as a mean for North American river water; seawater is approximately 19,000 ppm (0.54 M) in chloride [9]. Aquatic environments in the pH range of 6 to 8 are generally optimal for fish [10], and this is also the range in which methylmercury exhibits its greatest change in K_{ow} .

Observed increases in K_{ow} with increasing chloride concentration and decreasing pH are consistent with displacement of hydroxide by chloride on

the methylmercuric cation. Similarly, the near-zero K_{ow} of methylmercury in pure water and in saline solutions at high pH is attributed to a high proportion of methylmercuric hydroxide. From the behavior of the K_{ow} /salinity curve, we believe that the K_{ow} of methylmercury hydroxide is very nearly equal to the K_{ow} we observed with either species in ultrapure water and in test solutions at pH 12 (0.07 ± 0.05). Conversely, the K_{ow} of methylmercuric chloride (1.7 ± 0.2) is equal to the K_{ow} of the methylmercury equilibrium mixture at high salinity.

The constancy of K_{ow} values for methylmercuric chloride in the ionic strength range 0.0047 to 0.6 M may be attributed to the compound's high water solubility and small size.

The difference between the K_{ow} values for methylmercuric ion in pure water and in strong chloride solutions was $+1.6 \pm 0.2$. A difference of this magnitude should have some effect on bioconcentration. Bioconcentration factors of 0.03 and 0.84 were calculated for methylmercuric hydroxide and chloride in fish by means of the Arthur D. Little CHEMEST program [11]. This program is useful in estimating environmental behavior of compounds from their physical/chemical properties. Thus, the absorption of methylmercury compounds by aquatic organisms should be enhanced by increased salinity and by decreased pH. However, current estimations of bioconcentration were established with organic compounds that accumulate primarily in the fat, whereas mercury can also bind to sulfur. This property may provide additional sites of accumulation of mercury on sulfhydryls in protein and prove estimates of bioconcentration inaccurate.

REFERENCES

1. Mitchell, B.E. and B. Richards. 1986. Levels of chemical versus biological methylation of mercury in sediments. *Bull. Environ. Contam. Toxicol.* 36:401-404.
2. Stumm, W. and J.J. Morgan. 1981. *Aquatic Chemistry*, 2nd ed. John Wiley & Sons, New York, NY.
3. Hansch, C. and A.J. Leo. 1979. *Substituent Constants for Correlation Analysis in Chemistry and Biology*. John Wiley & Sons, New York, NY.
4. Lyman, W.J., W.F. Reehl and D.H. Rosenblatt. 1982. *Handbook of Chemical Property Estimation Methods: Environmental Behavior of Organic Compounds*. McGraw-Hill, New York, NY.
5. Shiochi, O. and S. Sokichi. 1985. The 1-octanol/water partition coefficient of mercury. *Bull. Chem. Soc. Jpn.* 58:3401-3402.
6. Wasik, S.P. 1978. Partition of organoelements in octanol/water/air systems. In F.E. Brinckman and

- J.M. Bellama, eds., *Organometals and Organometalloids*. ACS Symposium Series, Vol. 82. American Chemical Society, Washington, DC, pp. 314-326.
7. Corner, E.S. and B. Sparrow. 1957. Bioconcentration of mercury and methylmercury in marine fish. *J. Mar. Biol. Assoc. U.K.* 36:459-469.
 8. Altman, P. and D.S. Dittmer. 1966. *Environmental Biology*. Federation of American Societies for Experimental Biology, Bethesda, MD.
 9. CRC Press. *CRC Handbook of Chemistry and Physics*. 1985. CRC Press, Boca Raton, FL.
 10. Connell, D.W. and G.J. Miller. 1984. *Chemistry and Ecotoxicology of Pollution*. John Wiley & Sons, New York, NY.
 11. CHEMEST: Computer program for estimation of physical and environmental properties of organic compounds. 1985. Arthur D. Little, Cambridge, MA.

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